

## Effective repair to ultra-low-k dielectric material (k2.0) by hexamethyldisilazane treatment

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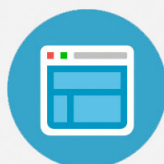
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# Effective repair to ultra-low- $k$ dielectric material ( $k \sim 2.0$ ) by hexamethyldisilazane treatment

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O<sub>2</sub> plasma ashing is commonly used to remove photoresist. The effect of O<sub>2</sub> plasma ashing on the porous organosilicate glass (CH<sub>3</sub>SiO<sub>1.5</sub>)<sub>n</sub>, one of the spin-on materials, is investigated. O<sub>2</sub> plasma can oxidize the methyl groups in porous organosilicate glass (POSG), which leads to the formation of Si–OH groups. The hydrophilic Si–OH groups will induce moisture uptake so that electrical degradation will occur in POSG film. Pure hexamethyldisilazane (HMDS) vapor (100% HMDS) can react with the Si–OH groups in POSG film. It converts hydrophilic Si–OH groups into hydrophobic Si–O–Si(CH<sub>3</sub>)<sub>3</sub> groups against moisture uptake. The leakage current density decreases by a factor of 2–3 and the dielectric constant decreases from 3.62 to 2.4 when O<sub>2</sub> plasma-damaged POSG undergoes HMDS treatment at 80 °C for 15 min. Therefore, HMDS treatment is the effective technique to repair the electrical degradation to POSG film during photoresist stripping processing.

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## I. INTRODUCTION

As circuit geometry is shrunk, the intrinsic circuit delay will increase due to the greater resistance in the metal interconnects, and also capacitance effects from the interconnects. Strategies to reduce so-called parasitic effects include incorporating metals with lower resistivity, such as copper, and providing an insulator with a low dielectric constant between the metal lines.<sup>1–4</sup>

Incorporating low dielectric constant (low- $k$ ) materials into deep submicron fabrication has received much attention in recent years. Many technical literatures have revealed various low- $k$  materials available with the dielectric constant in the range of 2.0–4.1.<sup>5–11</sup> According to the International Technology Roadmap for Semiconductors (ITRS),<sup>1</sup> by the year 2004 the minimum feature size will be 0.1  $\mu\text{m}$ , which requires insulation with a dielectric material having a dielectric constant  $k < 2.4$ . As a result, ultralow dielectric constant

materials ( $k \sim 2$ ) will be necessary for the integrated circuits generations after that.

Porous organosilicate glass (POSG) is a promising candidate as an ultralow dielectric constant material. The incorporation of voids reduces the dielectric constant of the film by lowering the overall material density,<sup>12–14</sup> so that it has potential to drive the dielectric constant as low as 2.0. In addition, the porosity (volume fraction of pores) of the POSG film is about of 50%. Therefore, POSG film has higher potential in ultra-large-scale-integrated, applications as compared with other dielectric materials. However, the dielectric properties of the POSG film will be deteriorated during photoresist (PR) removal processes.<sup>15,16</sup> In order to overcome the process issue, hexamethyldisilazane (HMDS) treatment is provided to improve the quality of the POSG film after the POSG film undergoes the PR removal process. In addition, O<sub>2</sub> plasma ashing have been investigated to realize the impact of integrated processes on the dielectric film quality. Furthermore, the electrical measurement and material analy-

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ses have been also used to evaluate the POSG film during the PR removal process.

## II. EXPERIMENT

The precursor of the porous organosilicate glass is one of the silica-based sol-gel materials, which is provided by the Chemat Inc. The POSG film,  $(\text{CH}_3\text{SiO}_{1.5})_n$ , has been developed by increasing the number of the methyl group, which causes the hydrophobic surface and results in the lower moisture uptake in the POSG film.

Unpatterned silicon wafers were coated with POSG solution at a rotational velocity of 3000 rev/min for 20 s. Then, a sequential bake was performed in the furnace under nitrogen atmosphere. For the bake condition, the temperature was raised from room temperature to 425 °C at a rate of 20 °C/min. Finally, the resulting wafers were further processed by furnace curing at 425 °C for 60 min.

In this work, Samples STD, O, and R were prepared. Sample STD was the as-cured POSG film without any plasma treatment. Sample O was the as-cured POSG film with O<sub>2</sub> plasma ashing for 30 s. Sample R was the O<sub>2</sub> plasma-treated POSG film (Sample O) after undergoing HMDS atmosphere at 80 °C for 15 min. Afterward, all of the samples were further processed by furnace curing at 400 °C for 60 min. Finally, aluminum was deposited onto samples STD, O, and R as the top electrode to manufacture the metal-insulator-semiconductor (MIS) structure.

The HMDS treatment was performed by utilizing HMDS vapor to treat sample O in an oven. The HMDS vapor is generated by heating HMDS solution and the vapor is conveyed to the oven at 80 °C. Moreover, the HMDS vapor treatment is carried out at a pressure of 760 Torr.

The O<sub>2</sub> plasma ashing was carried out in a plasma-enhanced chemical-vapor deposition chamber. The O<sub>2</sub> plasma was operated with a rf power density of 1.13 (W/cm<sup>2</sup>) at a pressure of 300 mTorr. The flow rate was 700 sccm, and the operated temperature was kept at 300 °C.

The chemical structure of the POSG film after different processes was investigated by Fourier transform infrared (FTIR) spectroscopy. The thickness of the POSG film was measured by an N&K analyzer 1200, which is a new type of thin-film measurement system. The N&K analyzer 1200, produced by N&K Technology, Inc., can measure the reflectance spectrum of the film. By comparing the resultant equation for theoretical reflectance with the actual measurement of reflectance, the thickness of the thin film can be determined. A Keithley Model 82 CV meter was used to measure the dielectric constant of POSG film and the capacitance-voltage (*C-V*) characteristic was measured at 1 MHz with an ac bias for high frequency. Finally, the current-voltage (*I-V*) characteristic was also measured by using the MIS structure to evaluate the insulation property of the POSG film.

## III. RESULTS AND DISCUSSION

In integrated processes, the photoresist removal is implemented conventionally by utilizing O<sub>2</sub> plasma ashing to re-

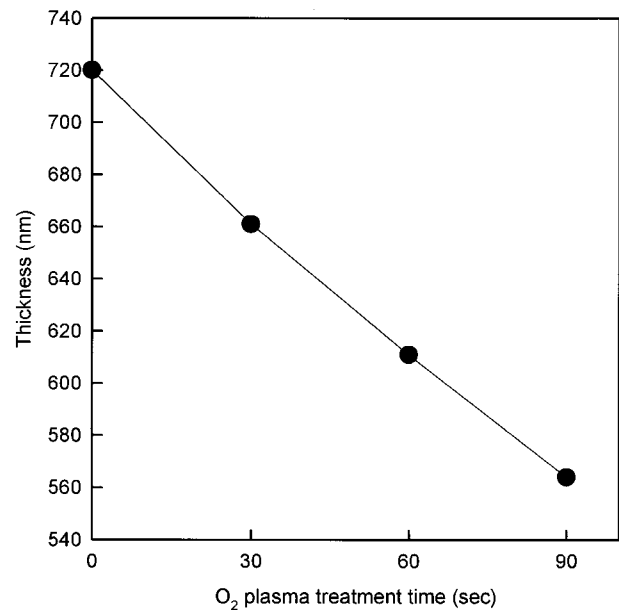
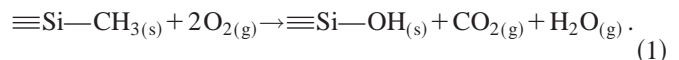


FIG. 1. Thickness variation of POSG films (sample STD) with O<sub>2</sub> plasma ashing for 30–90 s.

move organic photoresist. However, POSG film has a large exposed-surface area. This will raise the opportunity of reaction between the POSG film and O<sub>2</sub> plasma when the POSG film undergoes photoresist removal. O<sub>2</sub> plasma is an excellent oxidant, and thus it can oxidize methyl groups ( $\equiv\text{Si}-\text{CH}_3$ ) in the film via the reaction



Therefore, the impact of O<sub>2</sub> plasma processing on the POSG film must be investigated.

Figure 1 shows the thickness variation of the POSG film (sample STD) with O<sub>2</sub> plasma ashing for 30–90 s. The thickness of the POSG film is decreased with the increase of the O<sub>2</sub> plasma treatment time. The decrease of thickness results from a drop of the methyl groups' content, caused by O<sub>2</sub> plasma ashing, which can be confirmed by the FTIR spectra (in Fig. 2). The FTIR spectra of sample STD after O<sub>2</sub> plasma ashing for 30–90 s are shown in Fig. 2. Both the intensities of the Si-C peaks (847 and 1277 cm<sup>-1</sup>) and the C-H peak (2980 cm<sup>-1</sup>) are decreased dramatically. Furthermore, the intensities of the Si-OH and H<sub>2</sub>O signals (938 and ~3400 cm<sup>-1</sup>) increase when O<sub>2</sub> plasma ashing is applied to sample STD. It is believed that oxygen radicals can diffuse deeply into the porous inner structure of the POSG film to react with a large amount of Si-CH<sub>3</sub> groups, which causes the content of the Si-C and C-H groups to decrease. Oxygen radicals will immediately oxidize the Si-CH<sub>3</sub> groups for the duration of the reaction between the O<sub>2</sub> plasma and Si-CH<sub>3</sub> groups. Hence, the oxidation will convert the Si-CH<sub>3</sub> groups into Si-OH groups via Eq. (1). Since the Si-OH group is hydrophilic, moisture uptake is easily induced. As a result, the intensities of the Si-OH and H<sub>2</sub>O signals will increase after sample STD undergoes O<sub>2</sub> plasma ashing.

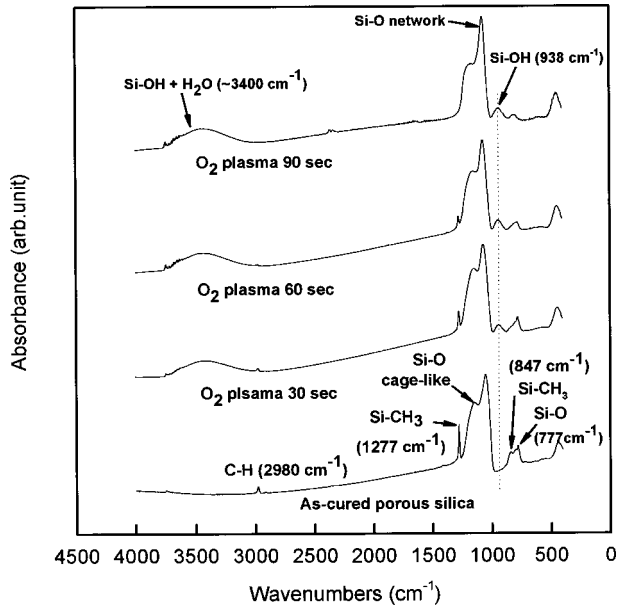


Fig. 2. FTIR spectra of POSG films (sample STD) with O<sub>2</sub> plasma ashing for 30–90 s.

The POSG film with an excellent low-*k* property is due to the higher density of the functional group. Therefore, when the function groups decompose after O<sub>2</sub> plasma treatment, dielectric degradation of the POSG film will occur. Figure 3 shows the dielectric constant variation of sample STD after undergoing O<sub>2</sub> plasma ashing for 30–90 s. The dielectric constant increases with the increase of the O<sub>2</sub> plasma treatment time. In addition, the leakage current also increases with the increase of the O<sub>2</sub> plasma treatment time, as shown in Fig. 4. These degradations are due to the formation of the Si–OH groups in the POSG film, as proved by the FTIR

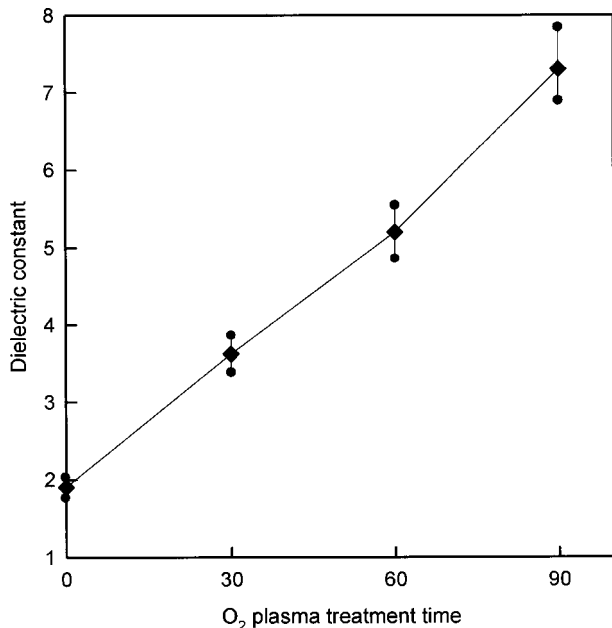


Fig. 3. Dielectric constant of POSG films (sample STD) with O<sub>2</sub> plasma ashing for 30–90 s.

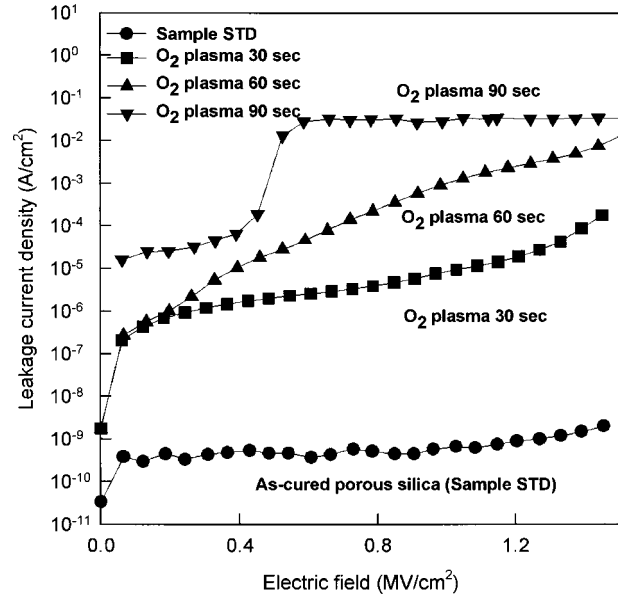


Fig. 4. Leakage current density of POSG films (sample STD) with O<sub>2</sub> plasma ashing for 30–90 s.

data. The POSG film with the Si–OH groups will easily absorb moisture. The high polarity of water molecules (dielectric constant  $\sim 78$ ) present in the POSG film gives rise to the increase of both leakage current and dielectric constant.<sup>17</sup>

In order to overcome the process issue, hexamethyldisilazane is provided to repair the damaged POSG film. The HMDS [(CH<sub>3</sub>)<sub>3</sub>Si–NH–Si(CH<sub>3</sub>)<sub>3</sub>] can eliminate the Si–OH groups via the reaction<sup>18</sup>

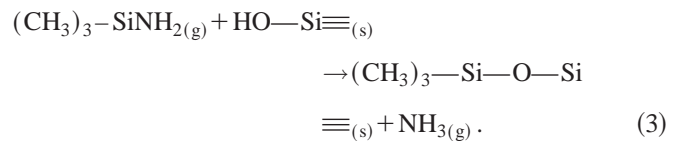
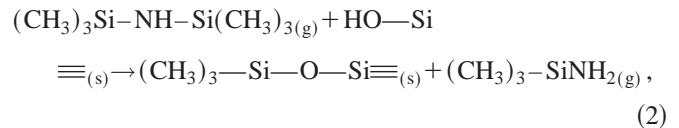
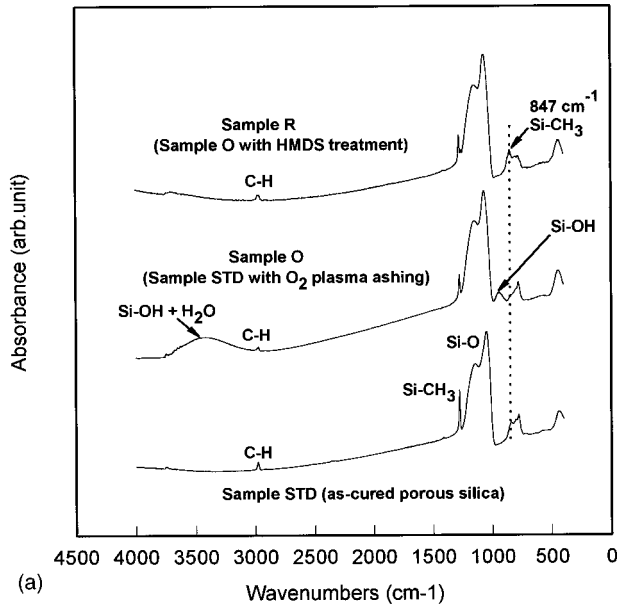
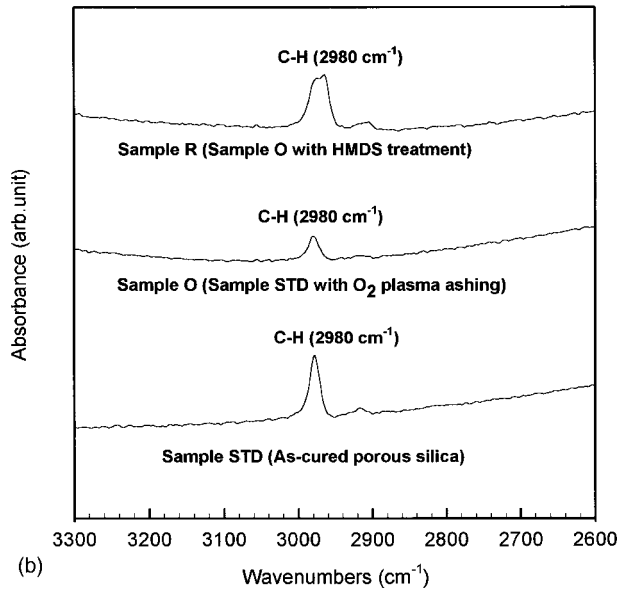


Figure 5(a) shows the FTIR spectra of samples STD, O, and R. In comparison with sample O (O<sub>2</sub> plasma-damaged POSG film), when sample O undergoes the HMDS treatment, the intensity of the IR bands from the Si–OH groups and moisture (938 and 3400 cm<sup>−1</sup>) decrease significantly, as shown in the spectra for sample R. Meanwhile, the intensity of the absorption band (847 cm<sup>−1</sup>) increases, which is characteristic for Si–C stretching and CH<sub>3</sub> rocking vibrations in trimethylsilyl groups [–Si(CH<sub>3</sub>)<sub>3</sub>], as shown in Fig. 5(a). In addition, Fig. 5(b) shows the variation of the intensity of the C–H groups. The Si–O peak appearing in the absorption band (1069 cm<sup>−1</sup>) is assigned to the reference peak. It is found that the peak-intensity ratio of C–H/Si–O on the FTIR spectra increases from 0.0359 to 0.0456 when the HMDS treatment is carried out on the oxygen-exposed POSG film, as shown in Fig. 5(b). These experimental results support our inference. The Si–OH groups are not only eliminated to re-



(a)



(b)

FIG. 5. FTIR spectra of samples STD, O, and R.

pair the damaged POSG film, but also undergo reaction with HMDS, which forms the Si–O–Si(CH<sub>3</sub>)<sub>3</sub> groups. Since the methyl groups are hydrophobic, the HMDS treatment can change the film surface from hydrophilic to hydrophobic.

Figure 6 shows the thickness variation of the POSG film with various process steps. The thickness decreases when the POSG film undergoes O<sub>2</sub> plasma ashing. The decrease of thickness results from a drop of the methyl group content, caused by O<sub>2</sub> plasma ashing. Nevertheless, the thickness of the damaged POSG film increases after further HMDS treatment, as shown in Fig. 6 for sample R. Two possible reasons may cause the increase of the thickness. One reason is that when HMDS reacts with Si–OH groups, it provides additional trimethylsilyl groups [–Si(CH<sub>3</sub>)<sub>3</sub>] to replenish the lost functional groups, caused by O<sub>2</sub> plasma ashing. The other reason is that some depositions of the HMDS species

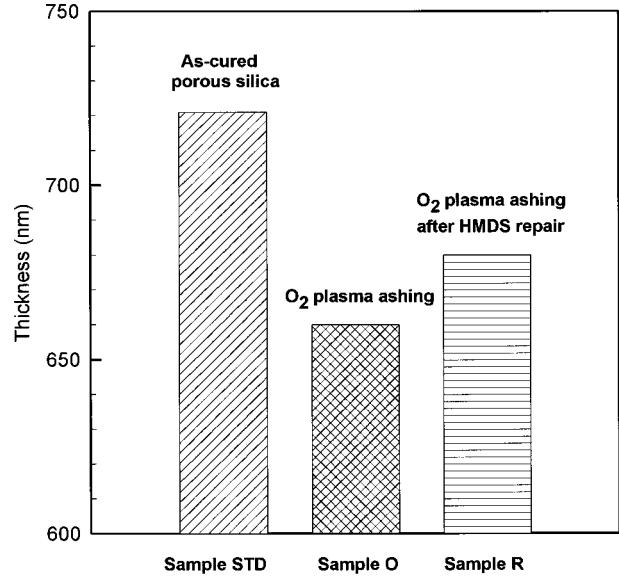


FIG. 6. Thickness of samples STD, O, and R.

are onto the surface of the damaged film. Therefore, the thickness of the POSG film will increase after the HMDS treatment.

Figures 7 and 8 show both the dielectric constant and leakage current variation of the POSG film when the POSG film undergoes O<sub>2</sub> plasma ashing and sequential HMDS treatment. The dielectric constant of the as-cured POSG film will increase after O<sub>2</sub> plasma ashing, whereas it decreases after sequential HMDS treatment. The dielectric constant of sample STD increases from 1.9 to 3.62 after O<sub>2</sub> plasma ashing, as shown in sample O. After sequential HMDS treatment, the dielectric constant decreases to 2.4, as shown in sample R.

Moreover, the leakage current density increases significantly when sample STD undergoes O<sub>2</sub> plasma ashing, as

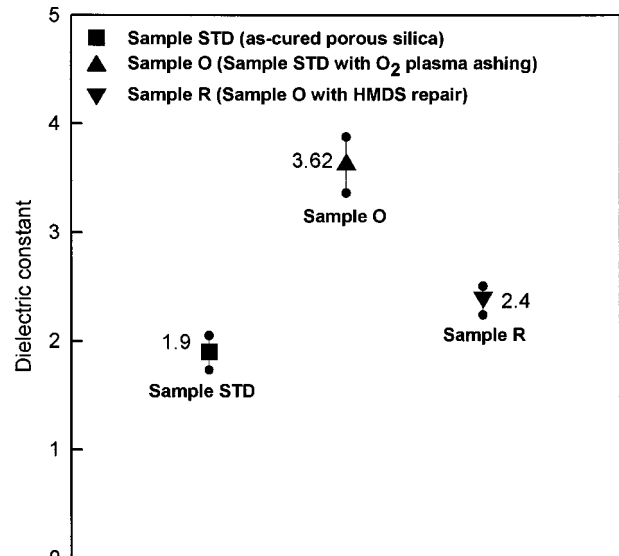


FIG. 7. Dielectric constant of samples STD, O, and R.

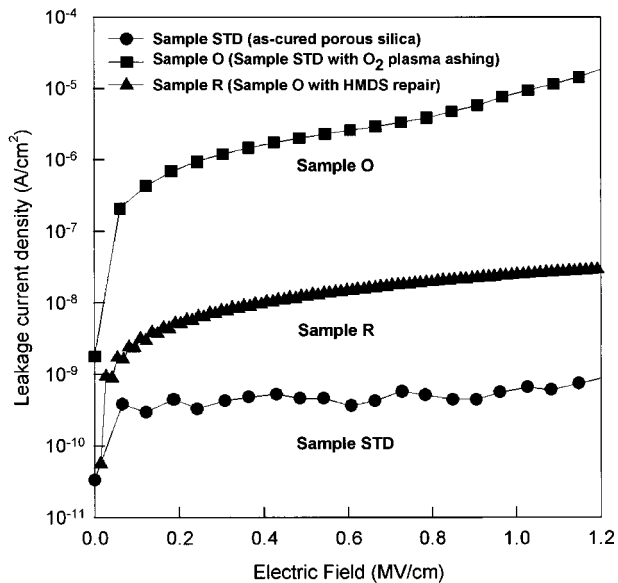


Fig. 8. Leakage current density of samples STD, O, and R.

shown in sample O. After further HMDS treatment, the leakage current density is decreased by a factor of 2–3, as shown in sample R. The electrical properties indicate that HMDS can repair the damaged structure and reduce both the leakage current density and dielectric constant of the POSG film.

#### IV. CONCLUSIONS

Electrical degradation will occur when the POSG film undergoes the O<sub>2</sub> plasma ashing processing. HMDS can repair the damage caused by O<sub>2</sub> plasma after the POSG film undergoes the photoresist removal process. Si–OH groups will be substituted by Si–OSi(CH<sub>3</sub>)<sub>3</sub> groups in the POSG film after the HMDS treatment. Si(CH<sub>3</sub>)<sub>3</sub> groups are hydrophobic so that the POSG film surface can be converted to become more hydrophobic. This will reduce the opportunity of moisture uptake and consequently both the leakage current and the dielectric constant will be decreased. As the result, the

HMDS treatment is an effective technique to repair damaged POSG film and has a higher potential for the photoresist removal application.

#### ACKNOWLEDGMENTS

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